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OXIDATION TECHNIQUES IN DRINKING WATER TREATMENT

PHYSICAL-CHEMICAL PRETREATMENT FOR THE REMOVAL OF PRECURSORS

J.M. Symons and A. A. Stevens

Papers presented at the Conference held in Karlsruhe, Federal Republic of Germany, September 11 - 13, 1978

Compiled and edited by

Dr.-Ing. W. Kühn and

Prof. Dr. H. Sontheimer

Karlsruhe, 1979

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PREFACE

This volume* contains the complete manuscripts of all lectures given by numerous leading scientists and engineers from many countries at the Conference on

"OXIDATION TECHNIQUES IN DRINKING WATER TREATMENT"

held in Karlsruhe, Federal Republic of Germany, in September 1978.

This conference was the tenth event in the series of lectures on special problems of water technology, held annually in turn at Berlin, Munich and Karlsruhe. It was also a meeting of the NATO-CCMS Study (CCMS: Committee on the Challenges of Modern Society) on Modern Problems of Drinking Water Supply.

Due to the participation of so many experts from different countries, these reports present a complete survey of all modern problems in the application of oxidation techniques in drinking water treatment. They also contain the latest results of practical and basic research as well as an outlook on future developments.

The editors wish to thank

- the German Federal Ministry of the Interior for the financial support
- the lecturers, discussion-leaders and -participants for the accurate preparation of their papers and for their valuable contribution to the conference
- the members of our Institute and of the DVGW Research Department who helped in organizing the conference, and
- Mrs. Ilse Hein and Mr. Bernd Frick for their help in compiling these reports for publication.

*One paper selected from this volume.

Karlsruhe, 1979

W. Kühn H. Sontheimer

PHYSICAL-CHEMICAL PRETREATMENT FOR THE REMOVAL OF PRECURSORS

J.M. Symons and A.A. Stevens

INTRODUCTION

The reaction of chlorine and precursors to yield chlorinated organics, as represented by Figure 1, would indicate three possible ways exist to attack the trihalomethane problem: 1) is the removal of the precursors by some treatment technique; 2) is to replace chlorine with some alternate disinfectant, or 3) is to remove the chlorinated organics once they are formed. This paper will review what is known about removal of precursor as a trihalomethane control procedure. Discussion of the other two techniques can be found elsewhere (1,2,3).

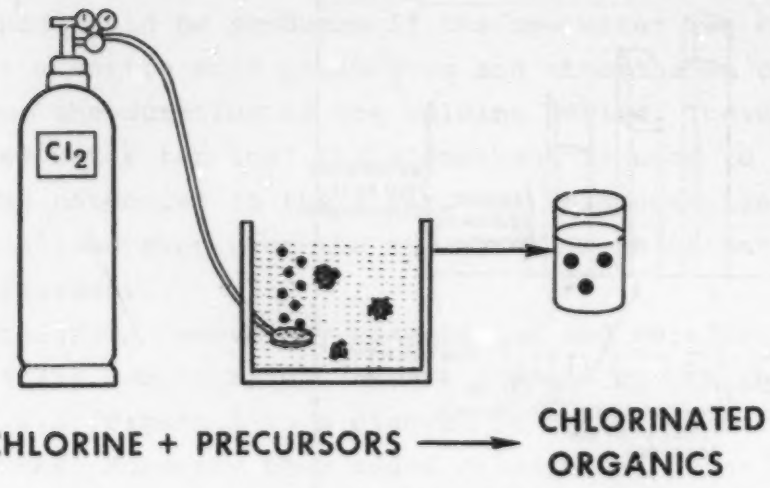

Fig. 1

REMOVAL OF PRECURSORS

For removal of precursors, three possible techniques have been explored: precipitation, oxidation, and adsorption, precipitation being either during lime softening or during turbidity and color removal with a coagulant, oxidation either with ozone, chlorine dioxide, or potassium permanganate, and adsorption either with powdered or granular activated carbon.

Precipitation

Pilot plant data would indicate that the amount of chloroform that is formed during treatment can be changed depending on the point of application of the chlorine (see Figure 2), either ahead of the flocculation basin, ahead of the filter, or after filtration. This

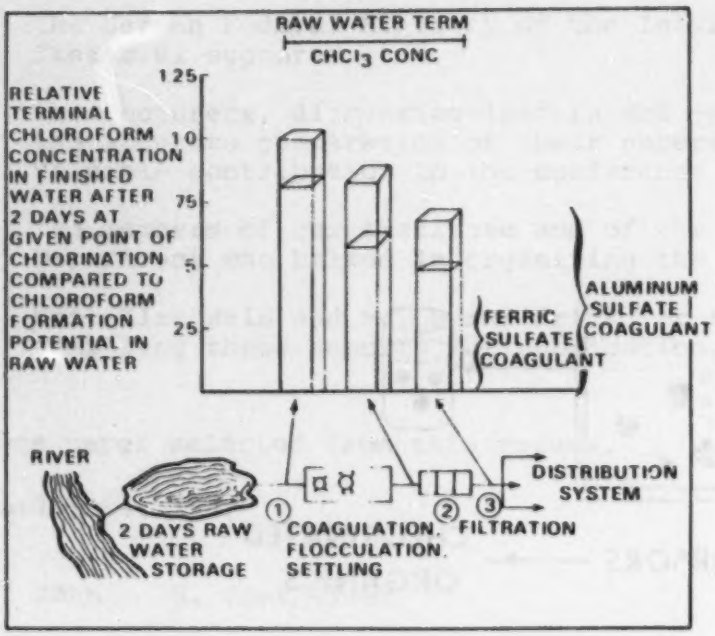

Fig. 2 Chloroform in finished water relative to point of chlorination (pilot plant studies)

indicates that precursors are being removed during treatment, and the later in treatment that chlorine is applied, the less chloroform is produced. In this particular water from the Ohio River, ferric sulfate was a more effective coagulant and so the solid part of the bars in Figure 2 indicates the ferric sulfate data, the total bar the aluminium sulfate data.

Raw water data are also indicated in Figure 2 for the terminal trihalomethane concentration and a question frequently arises as to why the raw water terminal trihalomethane concentration is higher than the amount of trihalomethane produced when raw water is chlorinated in a treatment plant. The explanation is that determination of terminal trihalomethanes is a test that is done in a bottle in which raw water and chlorine are mixed and held for some time and the resultant trihalomethane measured. In the treatment plant the chlorine is added, and as the water is passing through the coagulation and sedimentation basin the precursor and the chlorine are being separated by the settling process. Less trihalomethane is produced under these conditions than would be produced if the raw water was chlorinated in a bottle with precursors and chlorine in contact for the duration of the holding period. Therefore, the raw water terminal trihalomethane is used to indicate the potential in the water, but this potential is not realized even when the raw water is chlorinated during treatment.

Precursor removal by coagulation and settling was first (1975) demonstrated on a full scale at Cincinnati,Ohio, U.S.A. Figure 3 is a diagram of the Cincinnati Water Works. Formerly they added chlorine at point A, where chlorine and coagulant were both added. Then they moved the point of chlorination from point A to point B, the head end of the treatment plant. Because alum was added before presettling (point A), some particulate removal

occurred in these basins so the water quality at point B is considerably better than it would be at point A. The results of this change of chlorination practice are shown in Figure 4. After the point of application of chlorine was moved from point A to point B, the chloroform level dropped very dramatically.

In order to demonstrate that this was really caused by the moving of the point of application of the chlorine, and not because of a change in the river quality, the raw water trihalomethane formation potential was measured at various times throughout this period to show that precursors still did remain in the raw water. Even though a slight downward trend in concentration may have occurred through the winter months (Figure 4), it was certainly not equivalent to the dramatic drop in chloroform concentration that occurred when the point of chlorination was moved. Note that the brominated compounds did not change nearly as much in concentration on a percentage basis as did the chloroform.

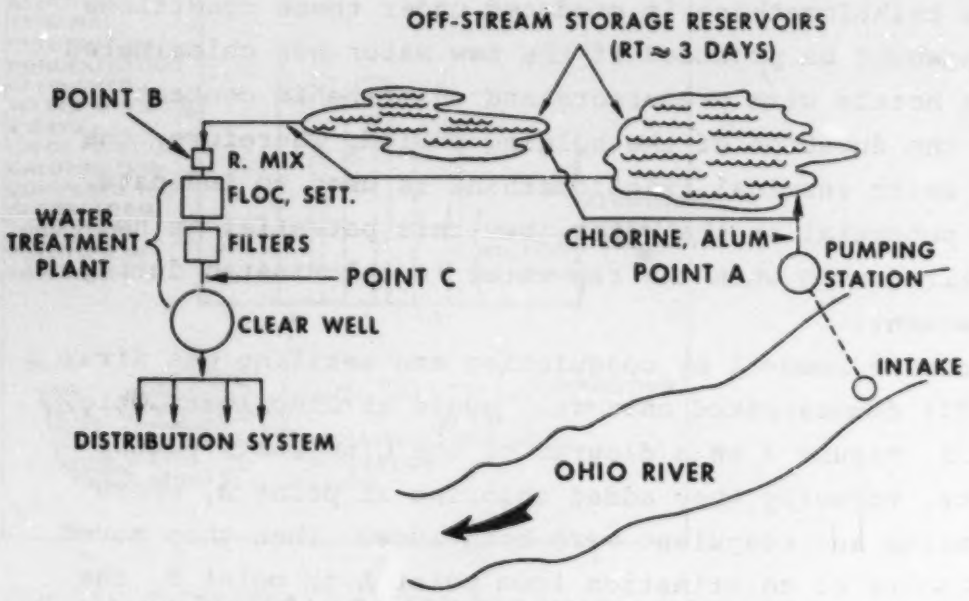

Fig. 3 Schematic of Cincinnati Waterworks

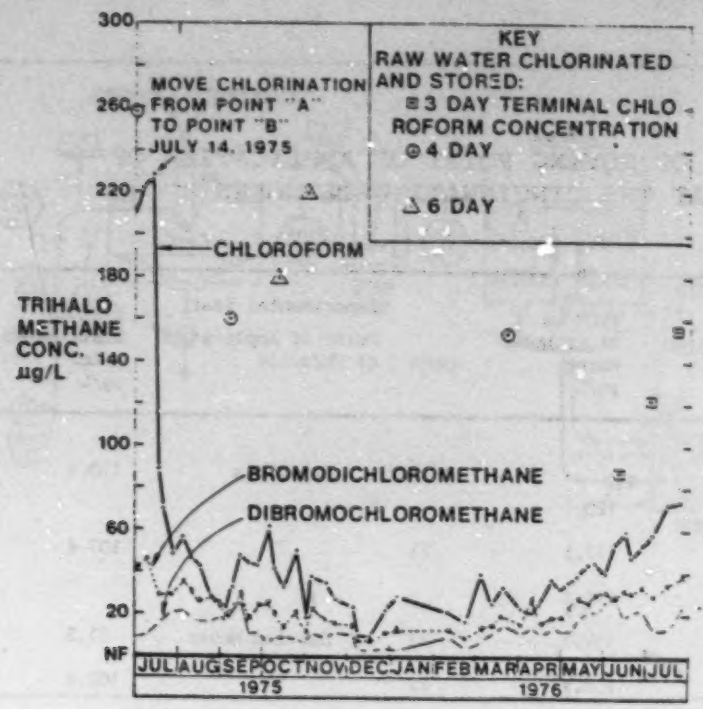

Fig. 4
Trihalomethanes in Cincinnati, Ohio tap water

Another trial was conducted in the late summer of 1977. In this case, the point of application of chlorine was moved from the rapid mix (hydraulic jump) to a point following sedimentation and before the rapid sand filters. Table I shows the trihalomethane concentration in the distributed water for 1976 during mid-September and early October and contrasts these data to those collected during the 1977 study. The generally lower concentrations during the 9/28/77-10/7/77 test again show the advantages of chlorinating as high a quality water as possible.

Figure 5 is a schematic diagram of the Daytona Beach, Florida, U.S.A., treatment plant. This utility did a study in which they chlorinated at three different points, 1) chlorinating the raw water, 2) adding chlorine at the recarbonation basin, and 3) adding chlorine at the clearwell. All of the trihalomethane concentrations were measured at sample point No. 5, which was several hours flow time following the clearwell.

TABLE I. INFLUENCE OF MOVING POINT OF APPLICATION OF CHLORINE AT THE CINCINNATI WATERWORKS

Date	Control Year Point of Application of Chlorine	THM in Distributed Water µg/L	Date	Experimental Year Point of Application of Chlorine	THM in Distributed Water µg/L
			9/13/77	Rapid Mix	120.8
9/16/76	Rapid Mix	120.1			
21	"	117.5	21	"	107.4
23	"	117.8			
28	"	119.7	28	Settled Water	81.5
29	"	108.9	29	"	102.4
30	"	115.8	30	"	76.0
			10/1	"	89.2
			- 2	"	87.4
			3	"	116.0
			4	"	78.1
10/5	"	109.7	5	"	77.7
			6	"	77.7
7	"	114.0	7	"	81.0
			10	Rapid Mix	112.9
			11	"	89.9
12	"	92.1			
14	"	109.0			

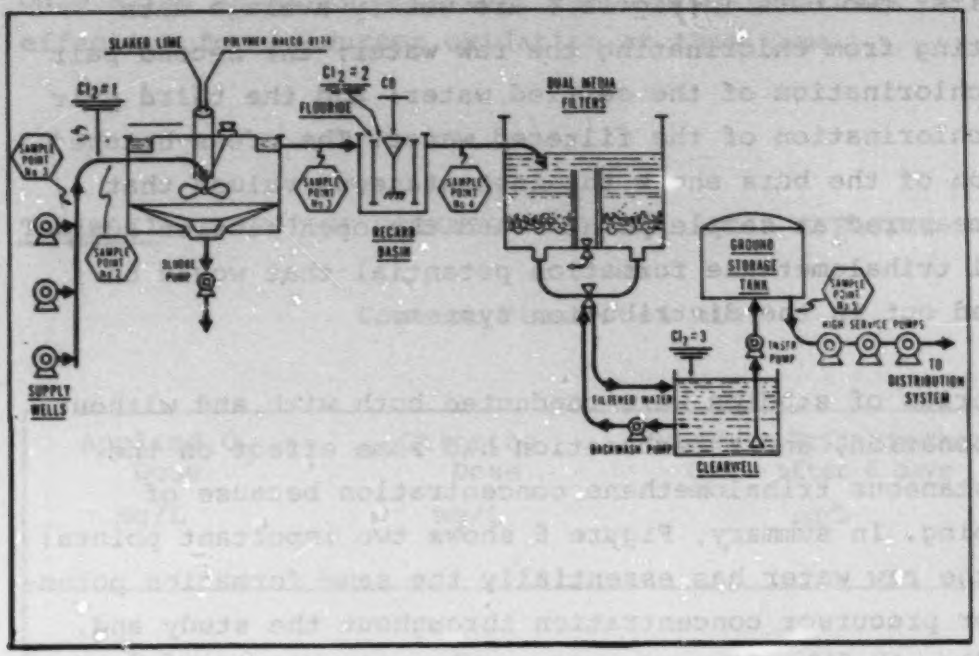

Fig. 5 Flow diagram Ralph F. Brennan Water Plant, Daytona Beach, Florida

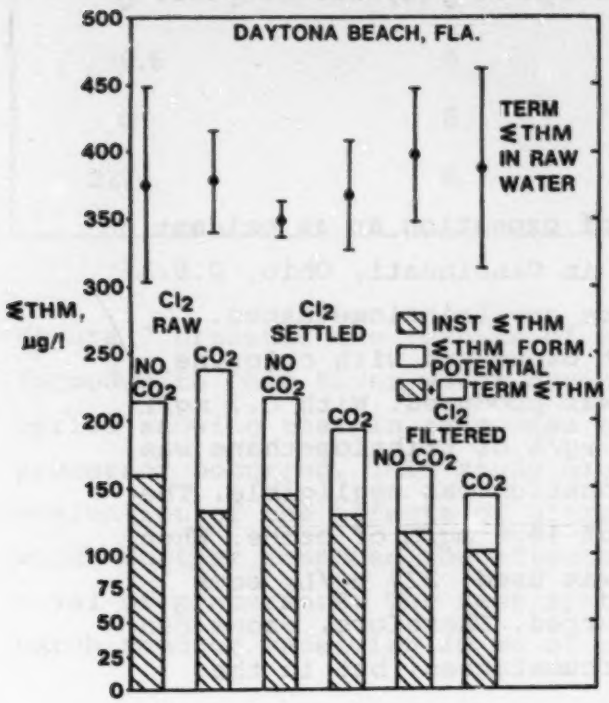

Fig. 6

The first two bars in Figure 6 are weekly average data resulting from chlorinating the raw water; the second pair from chlorination of the settled water; and the third pair from chlorination of the filtered water. The cross-hatched section of the bars shows the instantaneous values that were measured at sample point 5 and the open section additional trihalomethane formation potential that would be exerted out in the distribution system.

The series of studies were conducted both with and without recarbonation, and recarbonation had some effect on the instantaneous trihalomethane concentration because of stripping. In summary, Figure 6 shows two important points: one, the raw water has essentially the same formation potential or precursor concentration throughout the study and, secondly, the benefits of moving the point of application of chlorine are shown. The removal of precursor through coagulation and sedimentation was again demonstrated. The project is continuing in Daytona Beach attempting to demonstrate whether or not this effect can be improved even further through the use of the addition of polyelectrolytes.

Oxidation

- Ozone

Table II shows the effect of ozonation as an oxidant on pilot plant filtered water in Cincinnati, Ohio, U.S.A. Ozone alone does not produce any trihalomethanes. For the first study without ozone and with chlorine, 20 µg/L of trihalomethane was produced. With 0.7 mg/L of ozone plus chlorine, 23 µg/L of trihalomethane was produced. The effect of ozonation was negligible. The same occurred with a dose of 18.6 mg/L of ozone. When a very high dose of ozone was used, 227 mg/L, some oxidation of precursor occurred. Therefore, ozone can be effective in certain circumstances, but in the

Ohio River water it certainly was not particularly effective for precursor oxidation at this time.

Table II EFFECT OF OZONATION OF DUAL MEDIA EFFLUENT

Contact Time - 5-6 min.

Applied O_3 Dose mg/L	Chlorine Dose mg/L	Summation Trihalomethane Conc. after 6 days µg/L
0.7	0	< 0.2
0	8	20
0.7	8	23
18.6	0	< 0.2
0	8	23
18.6	8	30
0	8	123
227	8	70

Figure 7 presents the results of another study performed with Ohio River water during a different time period showing that in this case a big decline in precursor occurred. This study also included an evaluation of the effects of ultraviolet radiation which further enhanced the effects of ozone on removal of precursors. The test system was a 22 liter batch reactor receiving 20 mg of applied ozone per

minute. Although this study was also conducted on Ohio River water, the results were quite different from those shown in Table I.

The variability in the observed effect of ozone on trihalomethane precursor removed is further shown by Table III as compiled by Trussel. (4) These data from the independent work of several investigators range from negative removal to 90 percent. Several variables undoubtedly account for the observed wide range of results: nature of precursor, ozone dose, contact time, contactor design, including the dispersion system, and possibly other water quality factors.

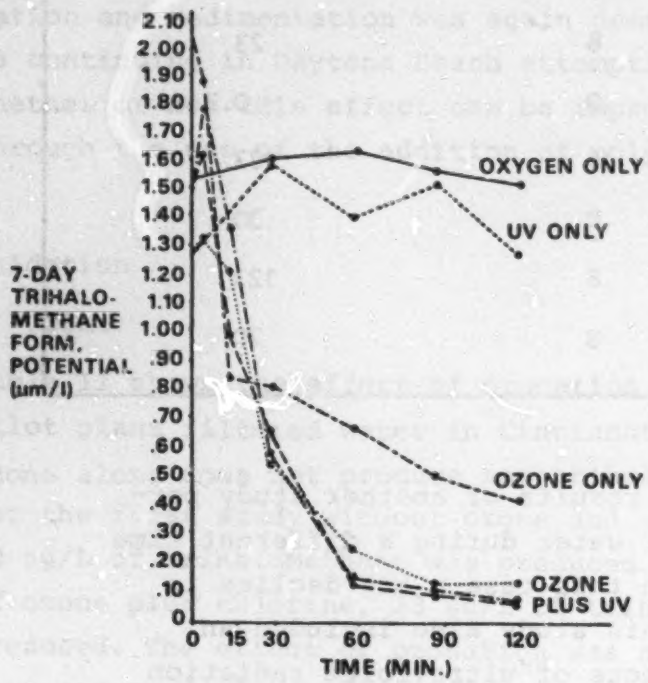

Fig. 7 Ozone and ozone-UV destruction of THM precursors Ohio river water (2/77)

Table III PRECURSOR REDUCTION WITH OZONE x)

Location	Dose, mg/L	% THM Precursor Reduction
Owens River	1.0	78
Lake Casitas	2.0	6
Columbia River	0.5	8
"	1.0	14
"	2.0	16
"	4.0	16
Ohio River	1.0	6
(Louisville)	2.0	22
"	4.0	30
"	6.0	46
"	8.0	46
Bay Bull's Big Pond	1.0	13
	2.0	19
	3.0	27
Ohio River		
(Cincinnati)	18.6	-31
	227	43
Mokelumne	2.0	62
	3.4	59
	4.5	59
	6.0	53
Middle River	2.6	-13
	2.8	- 3
	5.5	32
	10	7
	11	22
Rotterdam	2	60
	8	50
Orange County	1.0	7
Caddo Lake, Texas	0-72	0-90
Ohio River	0- 109	0-80

x) from R. Trussel, 1978 (4)

- Chlorine Dioxide

The data presented in Figure 8 show some removal of precursor by application of chlorine dioxide. The upper curve is the trihalomethane formation with chlorine alone, the middle curve is similar data with chlorine dioxide and the same amount of chlorine. The chlorine dioxide has some effect on the precursor such that it is changed so that it will not react with the chlorine to form trihalomethanes. The lower curve shows that chlorine dioxide alone does not produce trihalomethanes.

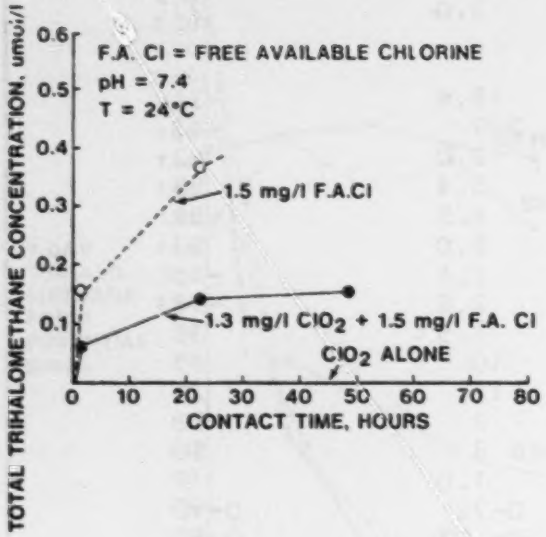

Fig. 8 Trihalomethane formation by ClO_2 and excess free available chlorine, ERC Pilot Plant settled water (6)

- Potassium Permanganate

Table IV presents the results of some preliminary studies investigating the effects of potassium permanganate on natural precursors from the Ohio River. In these experiments, the percent removals of precursor are relatively small, the highest is 19 percent, the lowest is 3 percent. Thus, potassium permanganate does not have large influence on the precursors that are in the Ohio River, although it does do some good. As mentioned in a previous paper (5), permanganate may have a more dramatic effect on precursors in some waters where precursors were observed to react more like m-dihydroxy phenyl moieties.

Table IV PRELIMINARY DATA ON PRECURSOR REMOVAL FROM OHIO RIVER WATER BY POTASSIUM PERMANGANATE

$KMnO_4$ Reaction			Chlorine Reaction Time (hours)	ΣTHM µg/L	% Removal
Amount Added (mg/L)	Reaction Time (hours)	pH			
0	1.5	7.1	2	30.5	
5	1.5	7.1	2	25.7	15.4
0	1.5	9.3	2	52.3	
5	1.5	9.3	2	50.9	2.7
0	1.5	10.2	2	57.2	
5	1.5	10.2	2	54.0	5.6
0	0.5	Neutral 7.0	30	120.5	
5	0.5	Neutral 7.0	30	97.6	19.0

Adsorption

- Powdered Activated Carbon

Figure 9 presents some typical data on the performance of powdered activated carbon (PAC) for precursor removal. In this experiment chloroform formation potential declined some initially, and then decreased more slowly as a 100 mg/L dose was approached. These data would tend to indicate that a 5 or 10 mg/L PAC dose would give an effect that might be favorable if a finished water had a trihalomethane concentration just above the proposed regulation, but PAC could not completely eliminate precursor even with an uneconomically high dose.

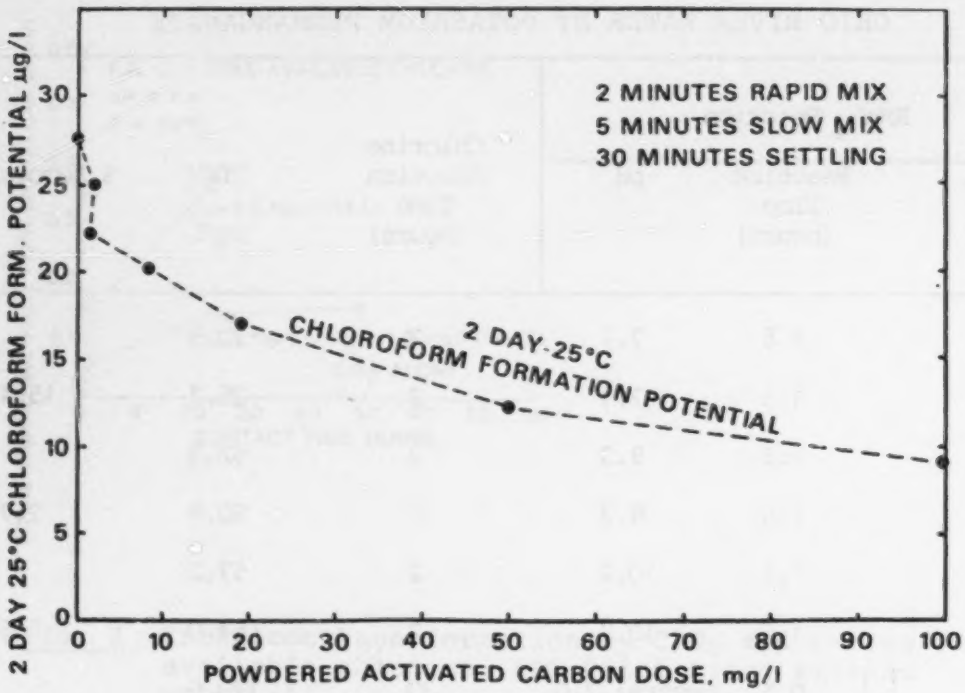

Fig. 9 Influence of powdered activated carbon on chloroform formation potential

- Granular Activated Carbon

Figure 10 shows data from a treatment plant in Huntington, West Virginia, U.S.A. The precursor is nearly completely removed initially and then the concentration steadily rises in the adsorber effluent, reaching the proposed maximum contaminant level (MCL) after about four weeks. Notice that the empty bed contact time here is only 6-1/2 minutes, which is a short empty bed contact time. Nevertheless, when the granular activated carbon is fresh, it will remove precursor well, but then a slow steady break-through occurs. Other data with deeper beds (longer empty bed contact time) tend to show that the time period for break-through to the proposed MCL is longer, Figure 11. Figure 12, data from the granular activated carbon treatment of water with a very high concentration of trihalomethane precursor, again demonstrates the influence of empty bed contact time.

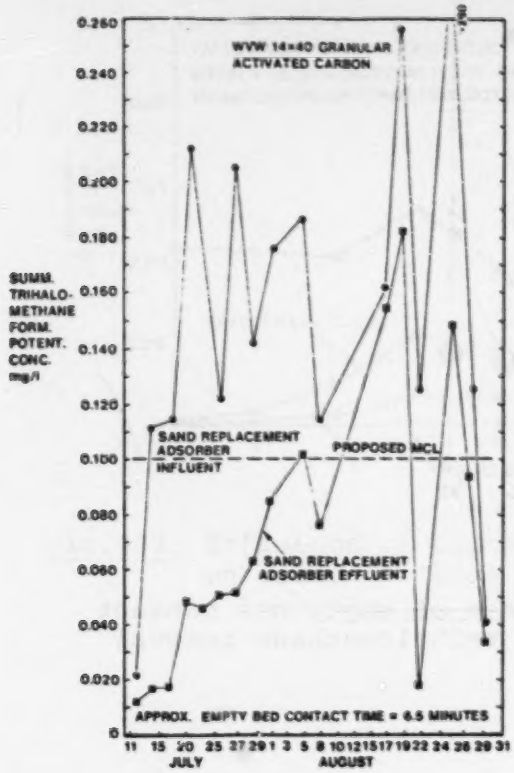

Fig. 10

Removal of trihalomethane precursors by granular activated carbon beds

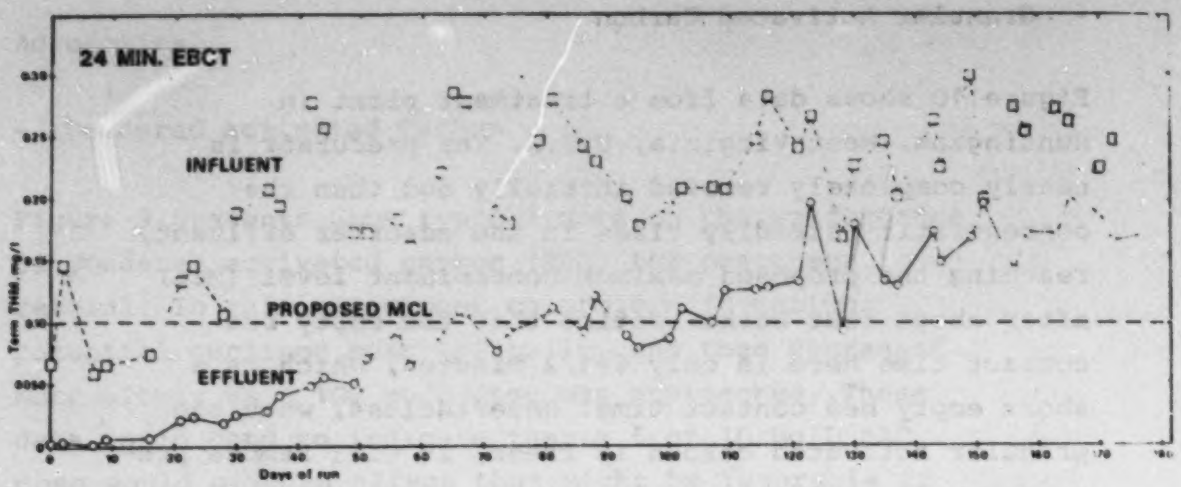

Fig. 11 Performance of terminal THM through Post Filter Adsorber run 1 (Feb.-Oct.1977) Jefferson Parish, La.

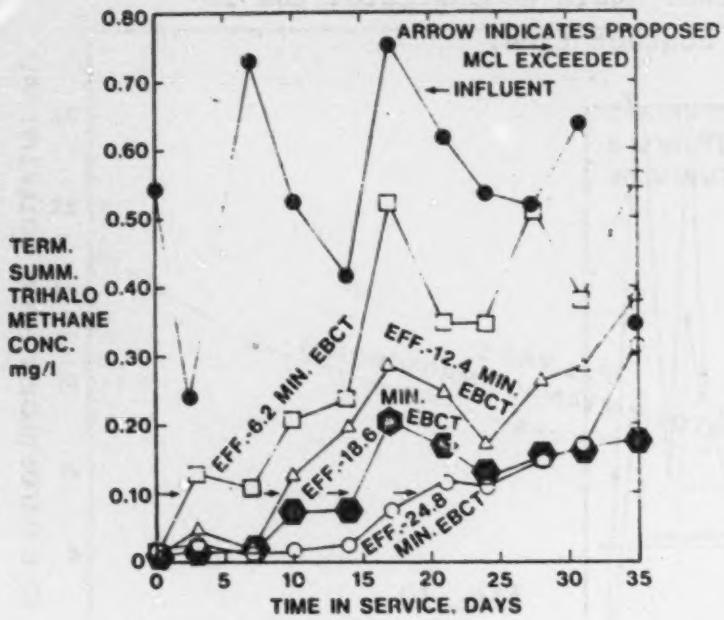

Fig. 12 Example of the influence of empty bed contact on terminal summation trihalomethane removal

- Ozone Enhanced Biologically Active Carbon Filters

A study on the utility of preceding granular activated carbon by ozone treatment on the removal of trihalomethane precursor was conducted in a pilot plant treating settled Ohio River water. The data in Figure 13 show that preceding the adsorption system by an ozone dose of about 1 mg/L, contact time 20 minutes, did result in a reduction in trihalomethane precursor in the adsorber effluent at any given service time when compared to conventional granular activated carbon. Both adsorption systems had a 9 to 10 minute empty bed contact time. The mechanism for this improved performance is thought to be related to an enhancement of biological activity in the activated carbon adsorber brought on by the ozone pretreatment.

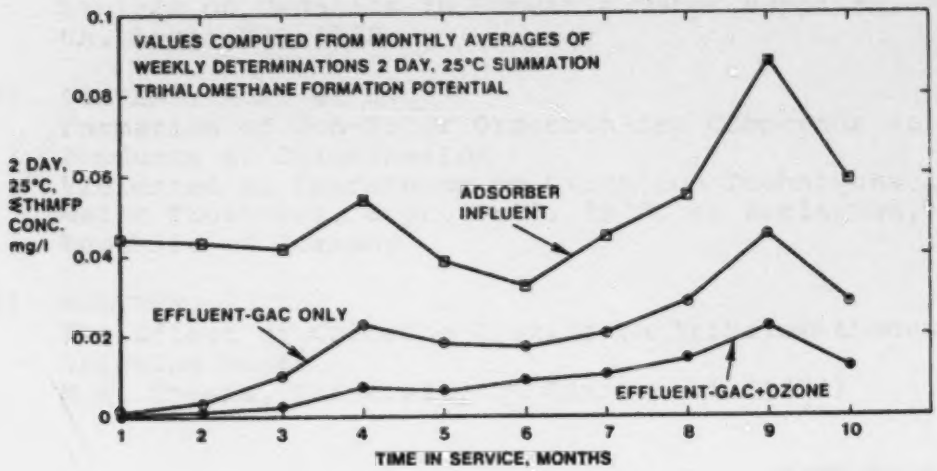

Fig. 13 Influence of ozonation prior to adsorption on trihalomethane formation potential removal

SUMMARY

Precipitation, oxidation, and adsorption are all methods of removing trihalomethane precursor. Of these various techniques, only adsorption on fresh granular activated carbon is completely effective, although the capacity of the activated carbon is finite. The other techniques, alum or iron coagulation, oxidation with ozone, chlorine dioxide or potassium permanganate, or adsorption with powdered activated carbon, are only partially effective but may still have a role in controlling trihalomethane concentrations in some cicumstances.

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